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N-ALKYLHETEROCYCLIC NITROGEN-CONTAINING DERIVATIVES AS CORROSION-INHIBITORS

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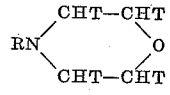
3 Claims. (Cl. 252—392)

This invention relates to the use of N-alkylheterocyclic compounds as corrosion inhibitors. More specifically, this invention relates to their use as corrosion inhibitors in static water and boiler water.

Corrosion of metallic substances represents a major industrial problem. Every year the loss to industry through corrosion amounts to millions of dollars. In general, this corrosion takes place when the metallic substances, especially ferrous-containing metals, come in contact with a watery media, i.e., water, aqueous solutions, water vapor and the like. Various methods are presently known and utilized for preventing or inhibiting the corrosive activity of the various aqueous media. The most frequently employed method for inhibiting and preventing corrosion is to cover the surface of the metallic substance with a protective coating.

It has now been discovered that a tenacious protective film of essentially monomolecular dimensions is formed when N-alkylheterocyclic compounds are contacted with the surface of the metallic substance. This film, as utilized in steam condensate lines, in addition to forming a protective coating over the surface, has a surface activity that maintains the heat transfer efficiency of the lines at their optimum.

Suitable compounds are represented by the general formula



where R is a straight chained hydrocarbon radical, and T is hydrogen or a lower alkyl radical. Preferably, T represents hydrogen and R represents an aliphatic hydrocarbon radical corresponding to the chain length of fatty acids in coconut oil, i.e., "coco," since these compounds are more effective than the other members of this class of compounds. It is noted that the heterocyclic nucleus in the above compounds is saturated, has a long chained aliphatic hydrocarbon radical attached to the nitrogen member of the ring, and the heterocyclic ring contains at least two dissimilar atoms other than carbon. These features are the salient characteristics of the compounds which are the exceptional corrosion inhibitors of this invention as will be shown hereinafter.

Thus, an object of this invention is to teach a family of compounds which possess an unusually high degree of effectiveness in divers corrosion inhibiting problems.

Another object of this invention is to teach a family of compounds which are more effective than presently employed compounds.

Specifically, in regard to protection of steam lines the compounds of this invention have sufficient steam volatility such that adequate quantities of the compounds are entrained in the steam to act as corrosion inhibitors in condensate return lines.

Furthermore, the salts of these compounds are liquids at room temperature. As such they may be metered directly as 100% active liquids without any trouble which greatly facilitates their ease of handling. This fact obviates any need for the preparation of stock solutions for sale to consumers and directly decreases freight charges in shipments to the consumer.

Other objects and advantages to this invention will become obvious upon reading the subsequent portions of the specification.

EXAMPLE I

The "static" water test and "dynamic" water test were employed to evaluate the effectiveness of the various compounds. The data obtained in these tests are empirical accelerated laboratory tests in which the corrosion effect is multiplied many times. For instance, in actual practice the systems would be closed systems whereas in the "dynamic" water test fresh air is constantly admitted into the system. The procedures followed in these tests are as follows:

Static water test

Step A.—1″×1″×1/16″ S.A.E. 1020 mild steel coupons having a 5/32″ diameter hole were pickled as follows:

(1) soak coupons in reagent grade acetone and dry in air.
(2) pickle 10.0 min. in concentrated HCl at room temperature with agitation.
(3) rinse in distilled water, acetone dip, dry at reduced pressure in desiccator and weigh to ±0.0002 gm. immediately.

Step B.—Suspend each coupon from a Pyrex hook in 150 ml. ±ml. of test solution (prepared from distilled water to ±1 p.p.m. inhibitor based on 100% active material) and control (distilled water) so as to be fully immersed with the coupon's top edge 1/8″ to 3/8″ below test solution surface using 250 ml. Pyrex Erlenmeyer flasks as a test container.

Step C.—Leave the coupon suspended for 7 days ±2 hours at room temperature.

Step D.—Remove coupons from test flasks and soak in inhibited 5% HCl at ambient temperature for 5.0 minutes to loosen scale.

Step E.—Lightly scrub each coupon with soft bristle brush and commercial-type detergent cleanser to completely remove corrosion products, but no base metal.

Step F.—Rinse coupons with distilled water, then acetone; dry at reduced pressure in desiccator and reweigh immediately.

Step G.—Calculate precent inhibition according to the following formula:

$$\frac{\dfrac{\sum_{i=n_c}^{i=1} C_i}{n_c} - \dfrac{\sum_{i=n_t}^{i=1} t_i}{n_t}}{\dfrac{\sum_{i=n_c}^{i=1} C_i}{n_c}}$$

i=individual test value
n=number of individual test values
c=percent weight loss of control coupon (identical test with no inhibitor present)
t=percent weight loss of test coupon

Dynamic test

Steps A and B are the same as in the static water test.

Step C.—Place 1000 ml. of test sample or control (distilled water) in a large round bottomed Pyrex flask used as a boiler pot and 500 ml. in the test chamber (500 ml. Pyrex Erlenmeyer flask) containing 3 coupons totally submerged and suspended from Pyrex hooks and adjust the test chamber so that this liquid level will be maintained with the overflow returning to the boiler pot.

Step D.—Heat the boiler pot so as to effect the steam distillation.

Step E.—Condense the steam and allow the condensate to enter the test chamber which is maintained at a temperature of 25 to 28° C.

Step F.—Simultaneous with the introduction of the steam condensate bubble purified air through the test chamber at the rate of 15 to 50 cc./second. The air is purified by passing compressed air through a charcoal purifier and distilled water prior to introduction into the test chamber.

Step G.—Carry out test over a 3 day period ±2 hours during which time the steam distillation is carried out about 8 hours out of each 24 hour period.

Step H.—Calculate percent inhibition according to the formula set forth in static water test.

In addition to testing the effectiveness of compounds as corrosion inhibitors, the dynamic test gives a good indication of the steam volatility and thermal stability up to 100° C. of the compounds being tested.

Table I lists the results obtained in the testing of various products according to the above procedures.

TABLE I

Compound	Static Water Test		Dynamic Water Test	
	Conc., p.p.m.	Percent inhibition	Conc., p.p.m.	Percent inhibition
N-dodecyl Morpholinium Oleate.	5	9		
	50	10	4	15
	100	12	500	100
	250	95		
	500	100		
N-coco Morpholinium Oleate.	50	5		
	100	10	4	30
	250	95		
N-dodecyl Morpholinium Acetate	250	3		
N-coco Morpholinium Acetate.	100	16	4	30
	500	21		
Octadecyl Amine Acetate	100	8	4	−2
	500	32		

EXAMPLE II

The continuous inhibition of steam condensate was tested with a 15 H.P. gas fired boiler (100 p.s.i. top operating pressure). The experiment was conducted with 90% of the steam being condensed and recycled. The other 10% was condensed and passed through three test chambers (containing the test coupons), then to the drain.

The feedwater was Minneapolis city water passed through a Zeolite bed (ion exchange resin). NaOH and tripolyphosphate were added at appropriate intervals for control of alkalinity and sludge formation, i.e. 30–60 p.p.m. phosphate and 400–500 p.p.m. methyl orange alkalinity.

The boiler had a capacity of 195 gallons and the feedwater and return condensate were collected in a 50 gallon make-up tank. Any chemical tested as a boiler additive was pumped into this make-up tank before entering the boiler.

Operating condition were:

45 p.s.i. steam pressure
160–164° F. return condensate temperature
140–140° F. make-up tank temperature
60–80° C. test chamber temperature
20 p.s.i.—feedwater pressure

The boiler was operated under these condition for 7 days to establish the rate of corrosion without any inhibitor present. This rate averaged between 8–10 mils per year. The inhibitor was added to the make-up tank water at low concentrations and gradually increased until corrosion was effectively stopped. The feed water pump and chemical feed pump were synchronized so that a constant concentration of inhibitor was maintained as new feedwater entered the system.

When the corrosion was stopped, the inhibitor supply was shut off to determine the life of the inhibitor film (by sampling a coupon each day).

The coupons used in the experiment were 1"×1"×1/16" mild steel coupons. The coupons were first treated by a 10 min. immersion in conc. HCl, a distilled water rinse, an acetone rinse, and vacuum dried. The coupons were then weighed and suspended in the test chambers. The post-treatment consisted of 5 min. immersion in inhibited 5% HCl to remove the scale, a detergent cleansing, water and acetone rinses, drying and weighing (the rate of corrosion was calculated based on the loss of weight of the coupons).

Results of this testing procedure are shown in Table II.

TABLE II

Inhibitor	Effective Conc.,[1] p.p.m.	Film Life,[2] days
coco morpholine acetate	16	5–7
octadecyl amine acetate	14	1

[1] Conc. required to obtain 90% or better inhibition.
[2] Time after stopping inhibitor feed for return to uninhibited corrosion rate.

EXAMPLE III

Dilute solutions of equal concentration containing coco morpholine acetate and octadecylamine acetate were aspirated into a steam line. The steam was subsequently condensed and contacted with test coupons. The octadecylamine gave 60–65% protection and the coco morpholine gave 90–92% protection as compared to the corrosiveness of untreated condensate.

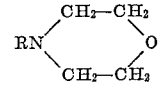
Accordingly, the morpholinium compounds of this invention are effective corrosion inhibitors when present in the aqueous media at concentration of 1 to 1000 parts per million.

It will be appreciated that the salts (total or partial) of these morpholinium compounds represent an easy and expedient means for facilitating their dispersion. On the other hand, other methods for adding in their dispersion, such as a colloid mill and the use of surface active agents, may be employed.

Therefore, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

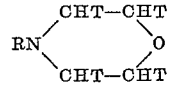
We claim as our invention:

1. A process for corrosion inhibition of ferrous substances intimately contacted by aqueous media which comprises adding to the aqueous media a fatty acid salt of a compound of the general formula,



where R is an aliphatic hydrocarbon radical and containing from 8 to 18 carbon atoms and covering said metallic substances with a tenacious protective film of said compound.

2. A process for corrosion inhibition of ferrous metallic substances intimately contacted by aqueous media which comprises adding to the aqueous media a fatty acid salt of a compound of the general formula,



where T is selected from the group consisting of hydrogen and aliphatic hydrocarbyl radicals containing less than five carbon atoms, and where R is an aliphatic hydrocarbon radical containing from 8 to 22 carbon atoms and covering said metallic substances with a tenacious protective film of said compound.

3. A process of preventing corrosion of ferrous metallic substances intimately contacted by aqueous media which comprises contacting said substances with N-alkyl morpholinium acetate where the alkyl radical is obtained

from coconut fatty acids and forming a protective film on the metallic substances with said compound.

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